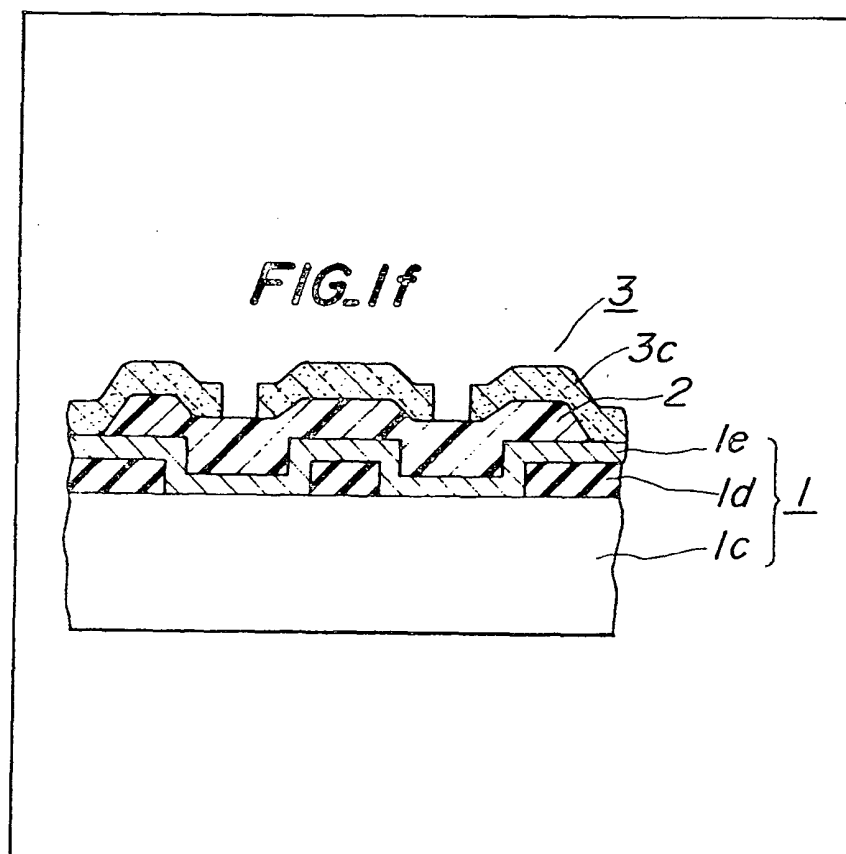


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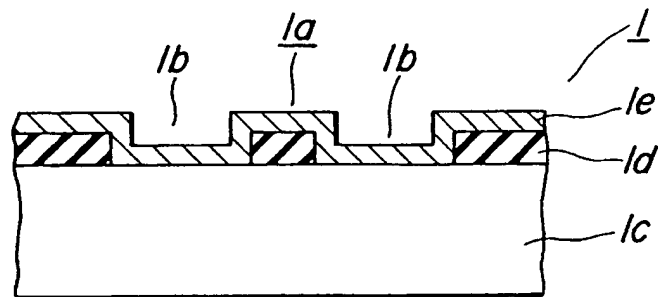
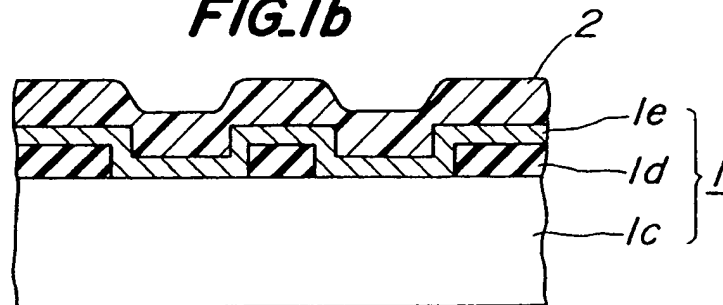
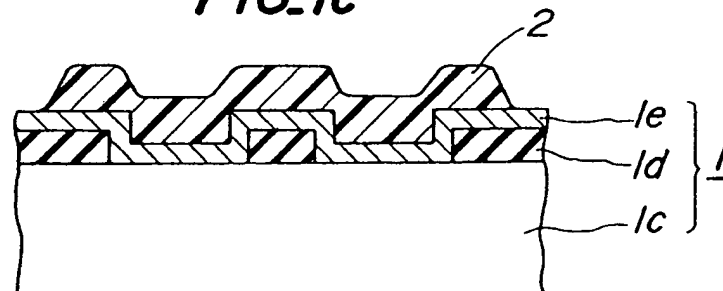
(54) Method of pattern formation

(57) In a method of pattern formation wherein an organic polymer resist material is simultaneously used with an inorganic resist material, a first desired pattern consisting of the organic polymer resist material layer (2) is formed on a substrate material, then the whole surface thereof is covered with the inorganic resist material layer (3), a second desired pattern is then formed with the inorganic resist material layer (3), and then the resulting second desired pattern is transferred to

the organic polymer resist material. The inorganic resist material layer consists of a selenium based glass sub-layer and a sub-layer containing silver. Mask alignment can automatically be effected by detecting reflected light from an alignment mark on the substrate, formation of a relief including large and small patterns is also easily carried out. The method of the invention may be combined with various process steps, so that such combined method is applicable for deep and shallow etching, formation of an interlayer insulation film, and lift-off method.

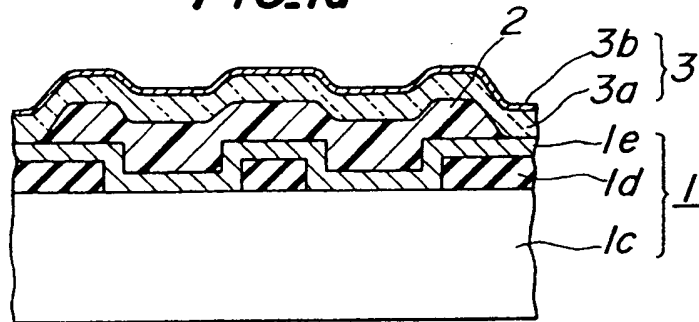


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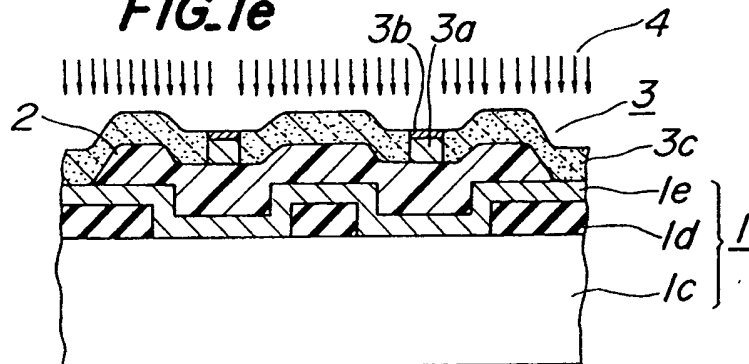
**FIG. 1a****FIG. 1b****FIG. 1c**

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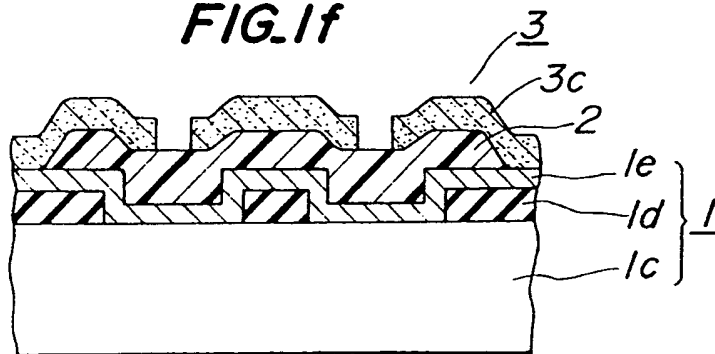
**FIG. 1d**



**FIG. 1e**

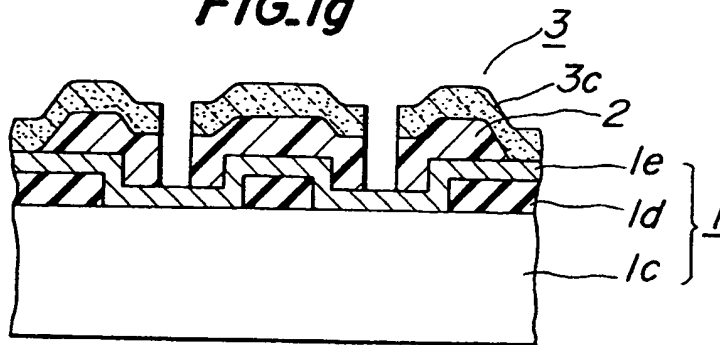


**FIG. 1f**

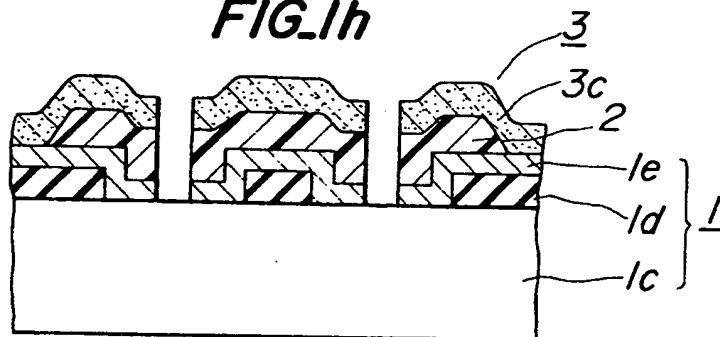


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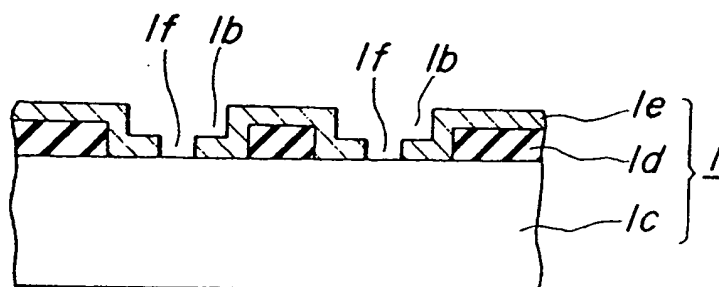
**FIG. 1g**



**FIG. 1h**



**FIG. 1i**



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FIG.2a

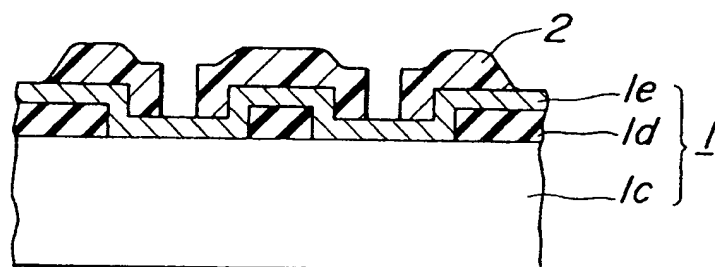


FIG.2b

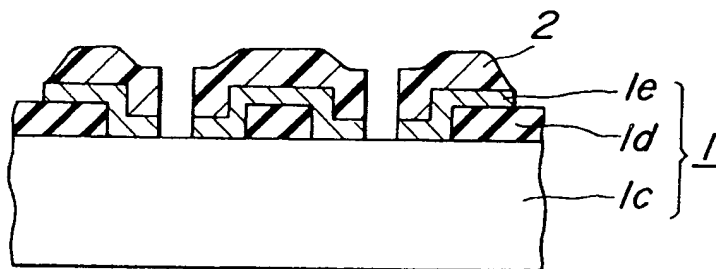
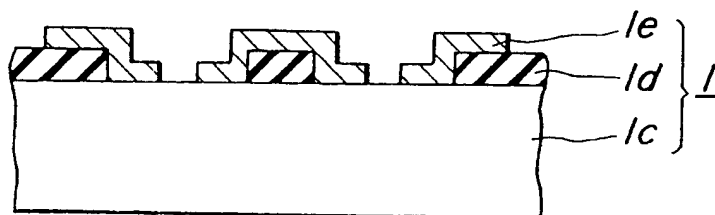
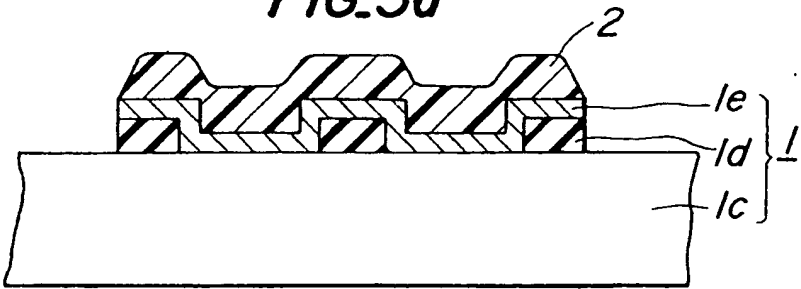


FIG.2c

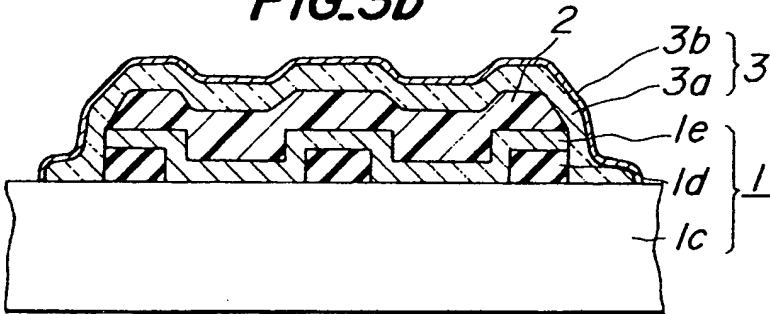


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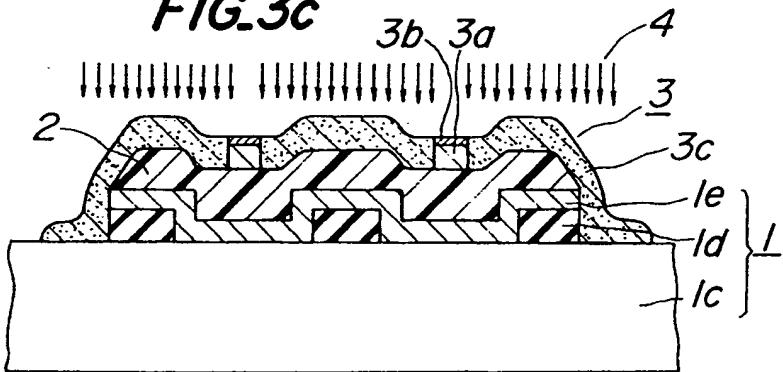
**FIG.3a**



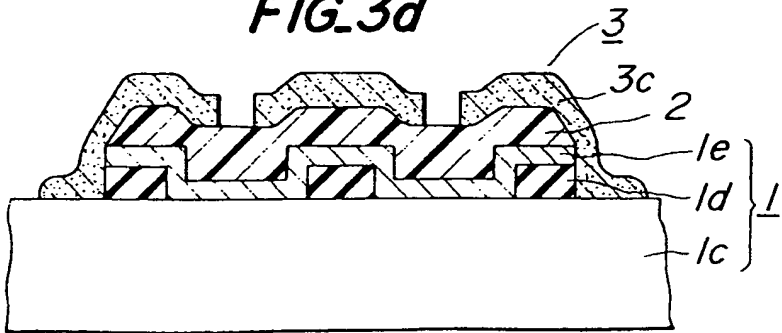
**FIG.3b**



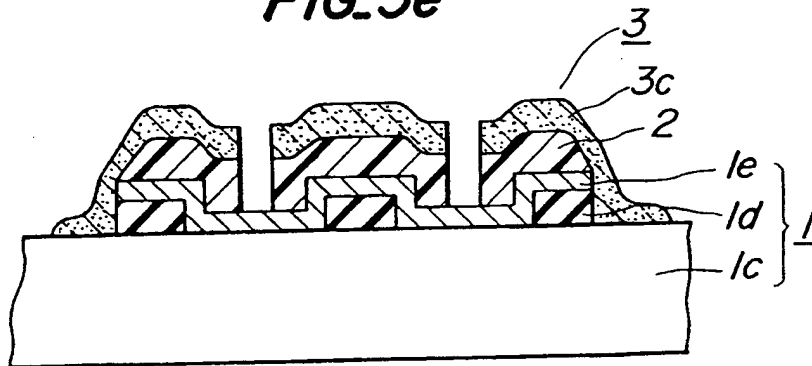
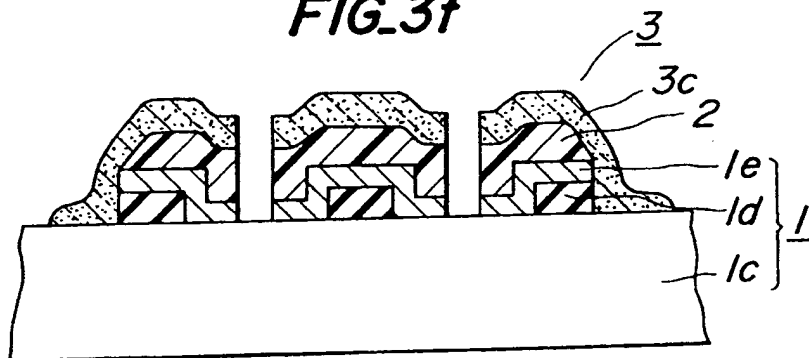
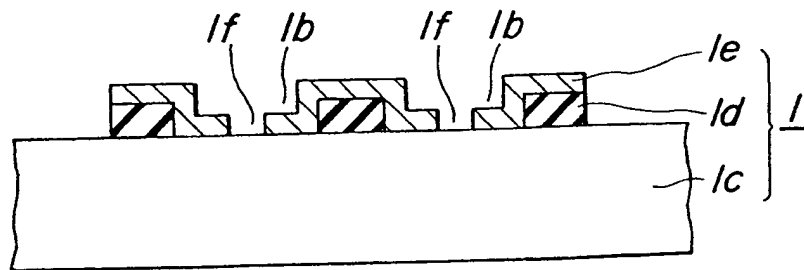
**FIG.3c**



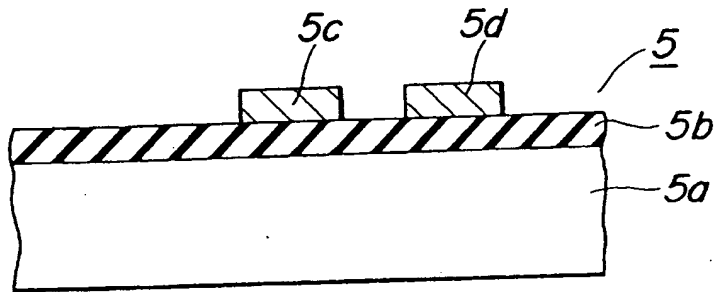
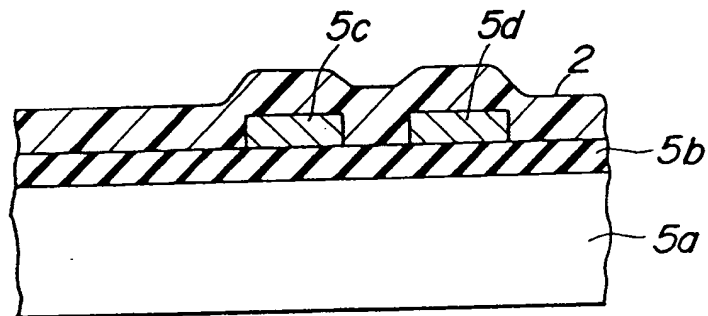
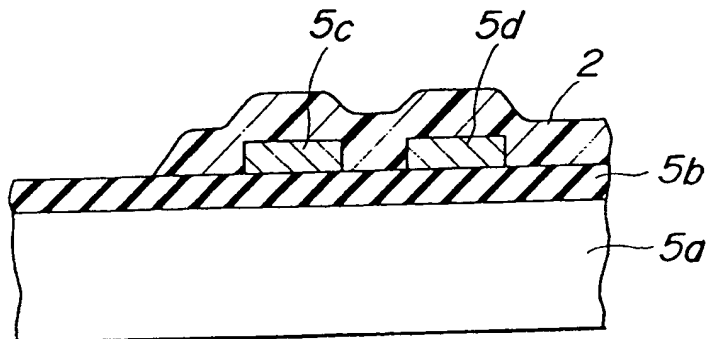
**FIG.3d**



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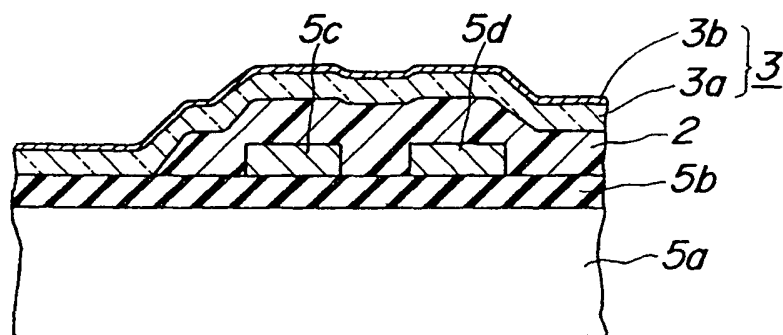
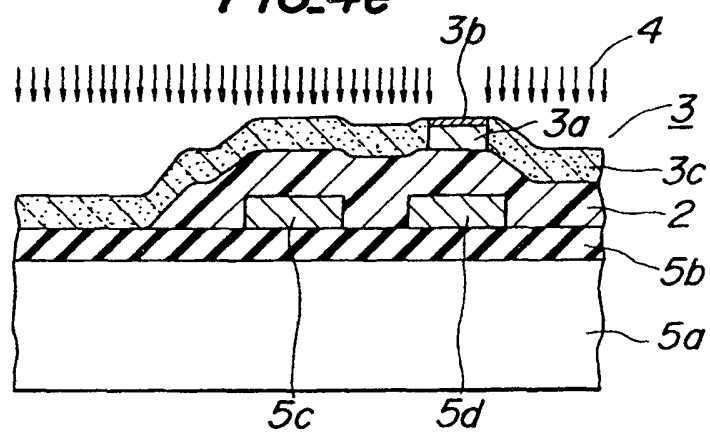
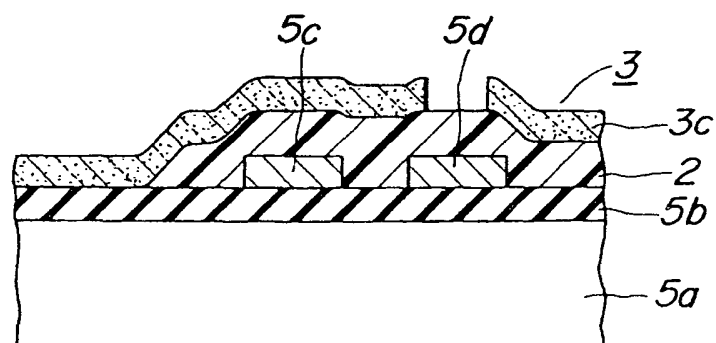
**FIG. 3e****FIG. 3f****FIG. 3g**

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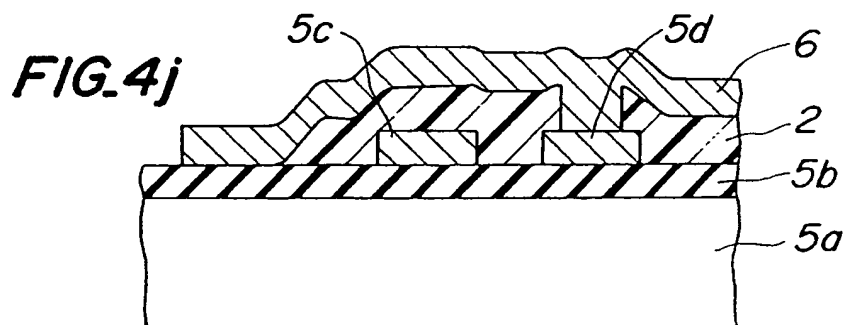
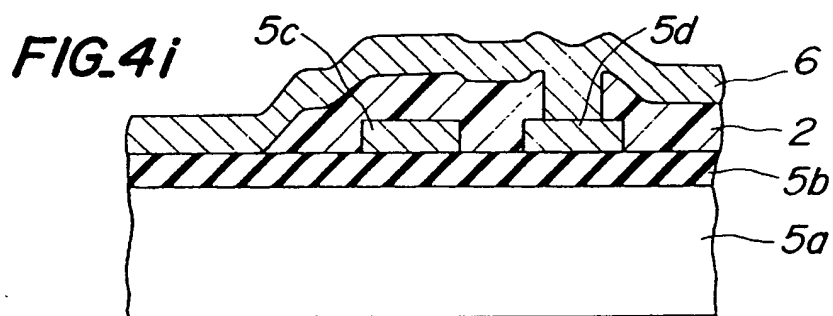
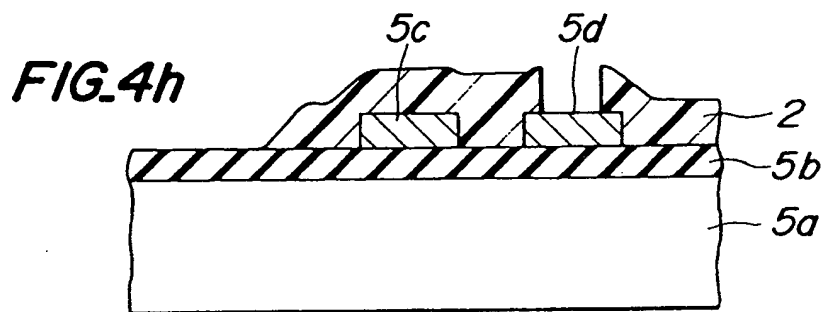
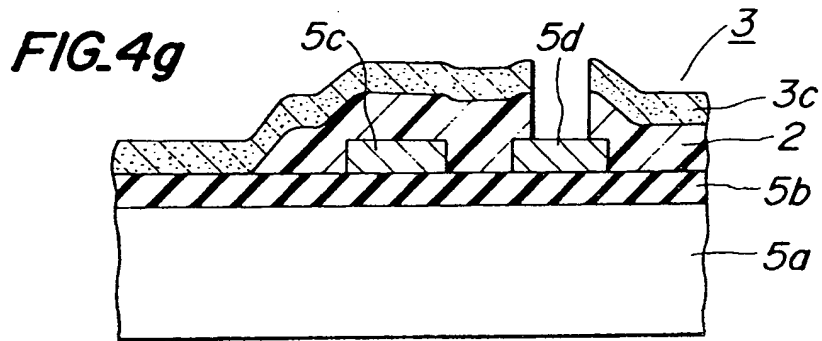
**FIG. 4a****FIG. 4b****FIG. 4c**



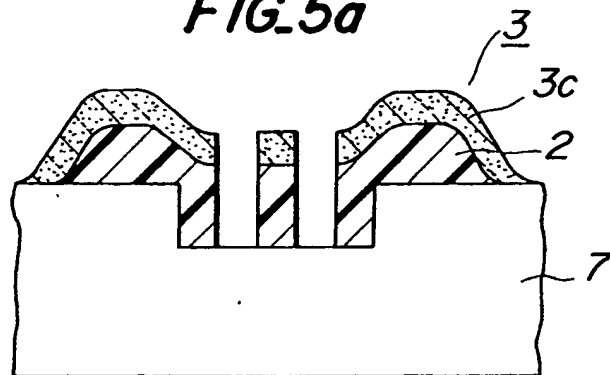
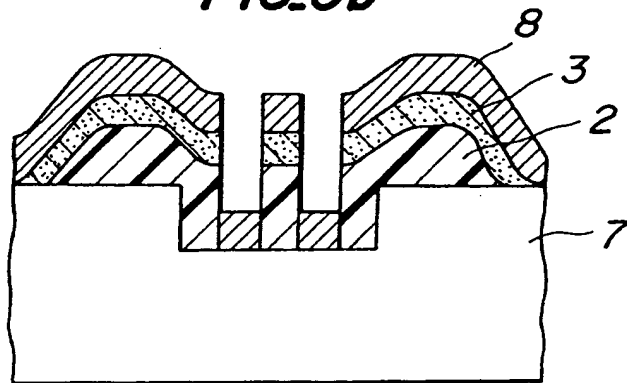
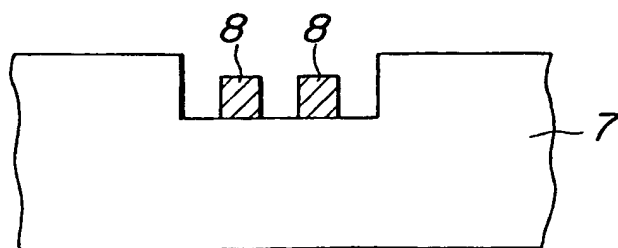
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**FIG.4d****FIG.4e****FIG.4f**

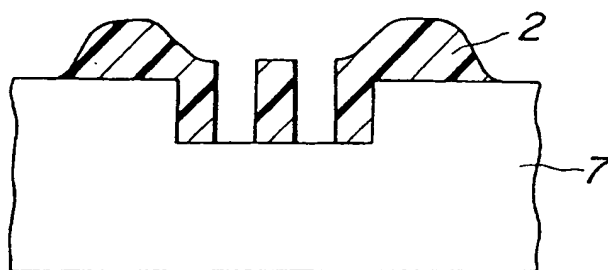
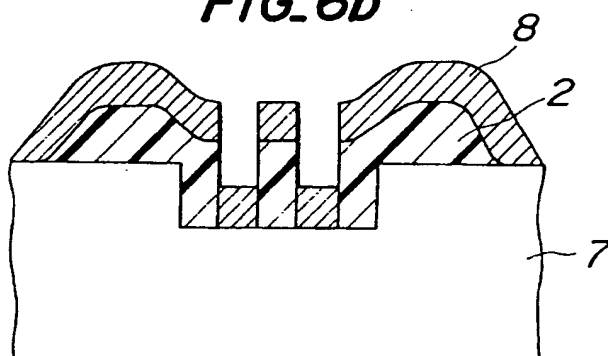
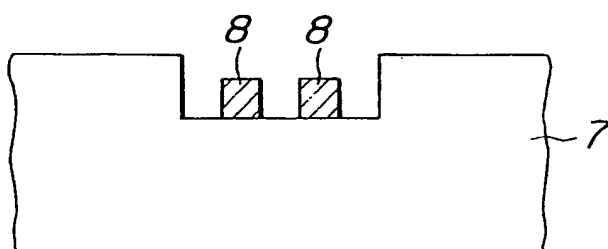
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**FIG. 5a****FIG. 5b****FIG. 5c**

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**FIG. 6a****FIG. 6b****FIG. 6c**

## SPECIFICATION

## Method of pattern formation

5 The present invention relates to a method of pattern formation which is utilized in the manufacture of semiconductor devices and the like.

Heretofore, a pattern formation in the manufacture of semiconductor devices, integrated circuits and the like has been mainly carried out in accordance with a photolithographic technology in which a photoresist made of a photosensitive organic polymer resist material is utilized. However, as a result of remarkable development in recent semiconductor devices and the like, as the most typically indicated in large scale integrated circuits, conditions required for pattern formation technique become very severe due to shrinkage of the size of elements in a device involved in the increase of the packing density of elements, growing of nonplanar features of surfaces of elements, diversification of materials to be etched, complication of multilevel interconnection, besides increase of ion stopping ability required for a mask for ion implantation with the increase of ion implantation energy and the like. Thus, such photoetching technique in which a conventional organic polymer resist material is utilized could not have complied with the requirements as mentioned above.

On the other hand, an inorganic resist material made of such a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing a silver compound or silver involved in an alloy or the like has recently been developed (see U.S. Patent No. 4,127,414), and this inorganic resist material has been attracted because of its many excellent characteristics including high resolution which are superior to those of a conventional polymer resist material. However, even if a customary photoetching is effected by the use of such inorganic resist material as described above, it is required that the inorganic resist material layer is extremely thinly formed in order to obtain the high resolution property. Accordingly, there still remains a problem in view of application property of such inorganic resist material to a nonplanar substrate surface or metal layer. Furthermore, since optimum conditions such as exposure, development and the like differ in the case where a relatively large pattern is formed from the case where a fine pattern is formed, there is such a problem in that a quality of patterns deteriorates as a whole in case of forming a relief including a large and small patterns.

In this respect, U.S. Serial No. 35, 803 (or corresponding Japanese Laidopen Patent Application No. 149, 941/1980 or European Patent Application Publication No. 0,018,653) "Process for fabrication of an article" as well as relevant papers "Bilevel high resolution photolithographic technique for use with wafers with stepped and/or reflecting surfaces" (J. Vac. Sci. Technol., 16(6), Nov./Dec. 1979, pp 1977 - 1979) and "Submicron optical lithography using an inorganic resist/polymer bilevel scheme" (J. Vac. Sci. Technol., 17(5), Sept./Oct. 1980, pp 1169 - 1176) disclose a bilevel resist prepared by laminating the above-mentioned inorganic resist onto an organic

polymer layer as a kind of multilayer resists. Such bilevel resist has the following advantages.

That is, flattening of a nonplanar substrate surface by means of the organic polymer resist material layer as well as formation of a fine pattern on a stepped or highly reflecting substrate by means of the inorganic resist due to its high optic absorption are easy. Furthermore, formation of a thick polymer resist pattern having a rectangular section is also easy and therefore, the aforesaid bilevel resist has a favorable application property with respect to a working in which a strong resistance is required for the etching mask such as reactive ion etching or ion beam etching working. The aforesaid process for the formation of the bilevel resist is also effective for a method of formation of mask pattern for ion implantation.

However, there still remains the following drawback in respect of the inorganic resist in also the pattern forming technique utilizing the bilevel resist. Namely, exposing and developing conditions in respect of the inorganic resist are different in case of forming a fine pattern from case of forming a comparatively large pattern. Consequently, if these conditions are suitably adjusted in the case when the fine and larger patterns are separately formed, it is possible to make qualities of these patterns equivalent to each other. In general, however, particularly in LSI, there are many cases in which these large and small patterns are included. In case of forming a relief including such large and small patterns, when the pattern formation of the above-mentioned bilevel resist is carried out under same exposing and developing conditions in respect of the inorganic resist in both the patterns, either or both of the patterns having unsatisfactory quality are formed. As described above, a relief including a large and small patterns cannot satisfactorily be formed by merely utilizing such bilevel resist.

In addition, there is a difficulty in alignment of a mask as an inherent problem of such bilevel resist. In a projection exposure system, getting popular is the alignment of mask which is automatically carried out by detecting the reflected light from an alignment mask on the substrate. However, as described above, the most advantageous points of the bilevel resist residue in flattening of a substrate surface and removal of the reflected light from the substrate. Therefore, no reflected light is obtained from the alignment mark covered with the bilevel resist, so that the above stated alignment of mask is impossible. Furthermore, in such bilevel resist, both of the polymer layer and inorganic resist layer are always treated as an integral member, but not either of them is individually patterned. In other words, there has been no consideration of such bilevel resist in respect of application to various pattern formations.

The present invention has been made in view of the above and an object of the invention is to eliminate the above-mentioned disadvantages and to provide a method of pattern formation which is widely applicable and has various pattern forming functions, besides the method by which a pattern with high resolution can be formed.

Another object of the invention is to provide a

method of pattern formation by which a multilevel interconnection pattern can be formed by utilizing the organic polymer resist material layer in a two-layer resist as an interlayer insulation film or layer.

- 5 Still another object of the invention is to provide a method of pattern formation by which a thin film pattern according to a lift-off process can suitably be formed by utilizing a two-layer resist.

10 In order to achieve these objects as described above, the method of the present invention comprises the steps of forming a first desired pattern consisting of an organic polymer resist material layer on the main surface of a material to be worked, applying a heat treatment to the patterned organic polymer resist material layer, forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material and a silver layer or layer containing silver on the organic polymer resist material layer thus heat-treated so as to cover the whole surface thereof, forming a second desired pattern with the aforesaid inorganic resist material layer, etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer, applying an etching treatment to the aforesaid material to be worked in a region which is not covered with the aforesaid organic polymer resist material layer, and removing the aforesaid inorganic and high polymeric organic resist material layers.

30 In the second aspect of the present invention, the method thereof comprises the steps of forming a first desired pattern consisting of an organic polymer resist material layer on the main surface of a material to be worked, applying a heat treatment to the patterned organic polymer resist material layer, forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver on the organic polymer resist material layer thus heat-treated so as to cover the whole surface thereof, forming a second desired pattern with the aforesaid inorganic resist material layer, etching to remove the polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer, removing the aforesaid inorganic resist material layer, applying an etching treatment to the aforesaid material to be worked in a region which is not covered with the aforesaid organic resist material layer, and removing the aforesaid organic polymer resist material layer.

50 In the third aspect of the present invention, the method thereof comprises the steps of forming a first desired pattern consisting of an organic polymer resist material layer on the main surface of a material to be worked, applying a heat treatment to the patterned organic polymer resist material layer, etching to remove the aforesaid material to be worked in a region which is not covered with the aforesaid patterned organic polymer resist material layer, forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver on the organic polymer resist material layer thus heat-treated and the exposed surface of the aforesaid material to be worked by means of the

aforesaid etching treatment so as to cover the whole surface of the aforesaid organic polymer resist material layer and the surface of the aforesaid exposed material to be worked, forming a second desired pattern with the aforesaid inorganic resist material layer, etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer, applying an etching treatment to the aforesaid material to be worked in a region which is not covered with the aforesaid organic polymer resist material layer, and removing the aforesaid inorganic and organic polymer resist material layers.

70 In the fourth aspect of the present invention, the method thereof comprises the steps of forming a first desired pattern consisting of an organic polymer resist material layer on the main surface of a substrate material provided with a patterned conductor layer, applying a heat treatment to the aforesaid patterned organic polymer resist material layer, forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver on the organic polymer resist material layer thus heat-treated so as to cover the whole surface thereof, forming a second desired pattern with the aforesaid inorganic resist material layer, etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer, removing the aforesaid inorganic material layer, and forming a third desired pattern consisting of a conductor layer of the aforesaid organic polymer resist material layer and the main surface of the aforesaid substrate material in a region which is not covered with the aforesaid organic polymer resist material layer.

90 In the fifth aspect of the present invention, the method thereof comprises the steps of forming a first desired pattern consisting of an organic polymer resist material layer on the main surface of a substrate material, applying a heat treatment to the patterned organic polymer resist material layer, forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver on the organic polymer resist material layer thus heat-treated so as to cover the whole surface thereof, forming a second desired pattern with the aforesaid inorganic resist material layer, etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer, forming a thin film layer on the aforesaid inorganic resist material layer and the main surface of the aforesaid substrate material in a region which is not covered with the aforesaid organic polymer resist material layer, and removing the aforesaid inorganic and organic polymer resist material layers together with the aforesaid thin film layer formed on the aforesaid inorganic resist material layer.

125 In the sixth aspect of the present invention, the method thereof comprises the steps of forming a first desired pattern consisting of an organic polymer resist material layer on the main surface of a substrate material, applying a heat treatment to the

patterned organic polymer resist material layer, forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver on the polymer resist material layer thus heat-treated so as to cover the whole surface thereof, forming a second desired pattern with the aforesaid inorganic resist material layer, etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer, removing the aforesaid inorganic resist material layer, forming a thin film layer on the aforesaid organic polymer resist material layer and the main surface of said substrate material in a region which is not covered with the aforesaid organic polymer resist material layer, and removing the aforesaid organic polymer resist material layer together with the aforesaid thin film layer formed thereon.

Furthermore, in the present invention, it is preferable that the aforesaid organic polymer resist material layer is made from a resist material comprising cyclized polybutadiene rubber as the principal constituent, while the aforesaid selenium-based glass material layer is made from a glass material comprising selenium and germanium as the principal constituents.

Figs. 1a - 1i are sectional views for explaining each stage in an embodiment of a method of pattern formation according to the present invention;

Figs. 2a - 2c are sectional views for explaining each stage in another embodiment of the method according to the invention;

Figs. 3a - 3g are sectional views for explaining each stage in a further embodiment of the method according to the invention;

Figs. 4a - 4j are sectional views for explaining each stage in still another embodiment of the method according to the invention;

Figs. 5a - 5c are sectional views for explaining each stage in a still further embodiment of the method according to the invention; and

Figs. 6a - 6c are sectional views for explaining each stage in yet another embodiment of the method according to the invention.

The method of pattern formation according to the present invention will be described in more detail hereinbelow with reference to the preferred embodiments thereof.

Figs. 1a - 1i are sectional views each showing a pattern in each stage of an embodiment of the method of pattern formation in accordance with the invention in which a window is established onto a recess 1b formed on the main surface 1a of a substrate material 1 as a material to be worked. Photoetching technique is very frequently applied to such a nonplanar surface in a manufacturing process of integrated circuits or the like. The substrate material 1 has, as shown in Fig. 1a, such structure obtained by disposing a first layer 1d made of a silicon oxide film formed to establish a prescribed pattern on the main surface of a semiconductor wafer 1c made of silicon by means of photoetching, and further placing a second layer 1e made of  $\text{SiO}_2$ , aluminium or the like on the main surface of the semiconductor wafer

1c so as to cover the whole surface thereof including the first layer 1d.

In case of providing a window on the recess 1b of the substrate material 1 having the structure as described above, first an organic polymer resist material layer 2 is formed on the main surface of the substrate material 1 so as to cover the whole surface thereof as shown in Fig. 1b. As such an organic polymer resist material, any material having a sufficient adhesion to the second layer 1e of the substrate material 1 irrespective of negative or positive type may be employed. For instance, all the resists possessing such trade names as CBR, KPR, OSR, OMR, KMER, KTFR, Waycoat, AZ and so on are preferable. Among others more preferable is a resist containing cyclized polybutadiene rubber as the principal constituent, for example, a negative photoresist CBR-M901 manufactured by Japan Synthetic Rubber Co., Ltd., because such type of photoresist has excellent heat-resisting properties. A film thickness of such resist may be within such an extent in which the resist does not produce pinhole, but can cover completely the nonplanar surface of the substrate material 1, i.e., it is preferable that such thickness is within a range of from around 1000 Å or more to several  $\mu\text{m}$  or less.

Pre-baking is applied to the organic polymer resist material 2 thus formed in accordance with a publicly known process, thereafter the organic polymer resist material layer 2 is exposed so as to leave at least a portion covering a nonplanar part of the substrate material 1, and the so exposed organic polymer resist material layer is successively developed in accordance with a publicly known manner to form a first desired pattern with the organic polymer resist material layer 2 on the main surface 1a of the substrate material 1 as shown in Fig. 1c. Then, the patterned organic polymer resist material layer 2 is subjected to heat treatment to cure the same. In this case, a required temperature is determined depending upon type of the resist material to be employed. For instance, a temperature within a range of about 200 - 250°C is preferable in case of utilizing CBR-M901. In the process of this heat treatment, the organic polymer resist material 2 presents softening and fluidizing phenomenon termed generally "resist flow". Accordingly, nonplanar surface in the main surface of the substrate material 1 is remarkably moderated on the surface of the organic polymer resist material layer 2, so that it is very advantageous for the succeeding formation of an inorganic resist material layer and photoetching.

Then, as shown in Fig. 1d, a selenium-based glass material layer 3a and a silver layer or layer 3b containing silver are successively laminated so as to cover the whole main surface of the substrate material 1 involving the organic polymer resist material layer 2 with which the first desired pattern is formed and the pattern is then subjected to thermosetting treatment in accordance with respective known processes to form an inorganic resist material layer 3 (see U.S. Patent No. 4,127,414). Thereafter, as shown in Fig. 1e, when the inorganic resist material layer is subjected to exposure with a second desired pattern by means of light or accelerated particle beam 4

such as electron beam or the like, the exposed portion of the selenium-based glass material layer 3a is doped with silver to form a silver doped region 3c.

Further, as shown in Fig. 1f, development is effected upon the substrate material by etching to remove the silver layer or layer 3b containing silver remained on unexposed portions of the inorganic resist material layer 3 and the selenium-based glass material layer 3a which is not doped with silver in accordance with a known manner and as a consequence, the second desired pattern can be formed by means of the inorganic resist material layer 3. As the selenium-based glass material constituting such inorganic resist material layer 3 as described above, any material presenting such doping phenomenon of silver upon exposure by means of the aforesaid light or accelerated particle beam 4 may be utilized, but a binary system glass material consisting of Se and Ge, particularly a material having such composition consisting of about 80 atom % of Se and about 20 atom % of Ge is preferable in view of resolution and sensitivity of the inorganic resist material layer 3. Moreover, a film thickness of such a selenium-based glass material layer 3a may be within an extent in which the layer can be formed without generating any pinhole thereon, and a preferable thickness is within a range from about several hundreds Å or more to 1 µm or less. Thereafter, as shown in Fig. 1g, etching is carried out by utilizing the inorganic resist material layer 3 on which the second desired pattern has been formed, i.e., the silver doped region 3c as a mask, thereby removing portions of the organic polymer resist material layer 2 which are not covered with the aforesaid mask. Such etching can be effected by a wet process in which a suitable solvent which can dissolve off the aforesaid organic polymer resist material is used, but dry etching by means of oxygen gas plasma, particularly an etching process having directional property as in reactive ion etching wherein a parallel flat plate-shaped plasma etching device is employed is preferable. In case of the latter process, the etching proceeds only along the direction of depth of the substrate material 1 and accordingly, there arises no undercut, so that a high resolution property involved in the inorganic resist material layer 3 is never damaged. Besides the selenium-based glass layer material has a very strong resistance with respect to such dry etching treatment by means of oxygen gas plasma, and therefore such selenium-based glass layer is very suitable for an etching mask.

As shown in Fig. 1h, the second layer 1e in the substrate material 1 is then etched by utilizing the inorganic resist material layer 3 formed to establish the second desired pattern and the organic polymer resist material layer 2 onto which the aforesaid pattern has been transferred as etching masks. The etching may be carried out by either a wet etching process by the use of a known etchant depending on the material of the second layer 1e, for example, if the second layer 1 is made of SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, an etchant buffer hydrofluoric acid or hot concentrated phosphoric acid is employed, or a dry etching process in which a publicly known gas suitable for the material of second layer 1 is utilized. As a result, it is also

possible that etching treatment for the organic polymer resist material layer 2 shown in Fig. 1g is carried out by a dry etching process in which oxygen gas is utilized, and another etching is successfully effected for the second layer 1e by merely replacing the oxygen gas by another etching gas in the same device.

Furthermore, developing treatment for the inorganic resist material layer 3 as shown in Fig. 1f may be effected by plasma etching in which a variety of freon gases is utilized, so that it is also possible to effect all the treatments for the inorganic resist material layer 3, the organic polymer resist material layer 2 and the second layer 1e shown in Figs. 1f, 1g and 1h, respectively, in the same etching device, whereby the process steps can remarkably be simplified.

Then, when the inorganic resist material layer 3 and the organic polymer resist material layer 2 are removed as shown in Fig. 1i, the substrate material 1 in the recess 1b in which a window 1f is formed can be obtained. In case of this removing treatment, any appropriate manner can be selected so far as the second layer 1e is not damaged, for instance, a method in which such treatment is carried out by the use of mixed solution consisting of sulfuric acid and hydrogen peroxide, or hot concentrated sulfuric acid, another method in which the inorganic resist material layer 3 is first removed by dipping the substrate material in weak alkaline solution for a long period of time, and then the organic polymer resist material layer 2 is removed by means of oxygen plasma, or the like method may be utilized.

In the above-mentioned embodiment, although such a case in which a window is established in recessed portions of the surface of the substrate material was merely described, the case directs only such a mode in which the method of pattern formation according to the present invention is applied to a nonplanar substrate surface. Accordingly, the invention is, of course, applicable for a variety of pattern formations, e.g., provision of window upon convex portions, provision of window on a substrate involving the stepped surface, and the like pattern formation to achieve the same advantageous effects as stated above.

Figs. 2a-2c are sectional views each showing a pattern in each stage of another embodiment of the method of pattern formation according to the present invention. In this embodiment, similar process steps for the treatment to that shown in Figs. 1a-1g are made before the process steps as shown in Figs. 2a-2c are carried out. Namely, as mentioned above, the first desired pattern is formed with the organic polymer resist material layer 2 on the substrate material 1, and then the second desired pattern is formed with the inorganic resist material layer 3 thereon to transfer the pattern to the aforesaid organic polymer resist material layer 2. Thereafter, the inorganic resist material layer 3 is removed as shown in Fig. 2a, and a layer to be worked on the substrate material 1, i.e., the second layer 1 is made of, for example, Al is then etched by utilizing the organic polymer resist material layer 2 as the mask as shown in Fig. 2b. Finally, when the remained



organic polymer resist material layer 2 is removed, a desired relief including large and small patterns can be formed as shown in Fig. 2C.

- As is understood from the above description, the present embodiment relates to a method in which the organic polymer resist material layer 2, which is utilized for merely covering and flattening a nonplanar substrate surface in the first embodiment shown in Figs. 1a-1i, is more positively used as an efficient mask for forming a relatively large pattern on the substrate material 1. By functionally dividing the method of pattern formation, in other words, if a fine pattern and larger pattern are formed on a substrate material by means of an inorganic resist and an organic polymer resist, respectively, it becomes advantageous to form such a relief involving a fine pattern within a region from several microns to submicrons and a larger pattern which does not require so high accuracy on a substrate surface. Such example is frequently found in case of a simultaneous formation of fine metalization pattern with bonding pad pattern of integrated circuits and the like cases, so that the method of the second embodiment is very effective for these cases.
- In the second embodiment, although such manner that the fine pattern formed with the inorganic resist material layer 3 is transferred to the organic polymer resist material layer 2, and then etching is applied to the layer to be worked in accordance with the larger pattern by utilizing the aforesaid organic polymer resist material layer 2 is specified, such manner may be somewhat modified. For instance, a larger pattern is formed with the organic polymer resist material layer 2 as shown in Fig. 1c, and then the second layer 1e and the first layer 1d being the layers to be worked are subjected to an etching treatment to remove the layers 1e and 1d which are not covered with the patterned organic polymer resist material layer 2 as shown in Fig. 3a.
- Thereafter, as shown in Fig. 3b, the inorganic resist material layer 3 consisting of the selenium-based glass material layer 3a and the silver layer or layer 3b containing silver is formed on the whole main surface of the patterned organic polymer resist material layer to which thermosetting treatment is applied as well as the surface of the material to be worked which is exposed by the etching treatment, i.e., the main surface of the substrate material 1 (semiconductor wafer 1c in Fig. 3b) so as to cover both the surfaces. Then, when exposure is carried out with a desired fine pattern by means of light or accelerated particle beam 4 such as light electron beam or the like, the selenium-based glass material layer 3a in the exposed portion is doped with silver to form the silver doped region 3c as shown in Fig. 3c. Furthermore, development is made on the substrate material by etching to remove the silver layer or layer 3b containing silver remained on unexposed portions of the inorganic resist material layer 3 and the selenium-based glass material layer 3a which is not doped with silver in accordance with a publicly known manner, whereby a fine pattern is formed with the inorganic resist material layer 3 as shown in Fig. 3d.
- Then, etching is carried out by utilizing the finely

patterned inorganic resist material layer 3, i.e., the silver doped region 3c as a mask to remove a portion of the organic polymer resist material layer 2 which is not covered with the mask, whereby the fine pattern is transferred to the organic polymer resist material layer 2 as shown in Fig. 3e. Thereafter the second layer 1e on the substrate material 1 is etched by utilizing the finely patterned inorganic resist material layer 3 and the organic polymer resist material layer 2 to which the above described fine pattern has been transferred as a mask as shown in Fig. 3f. Finally, the inorganic resist material layer 3 and the organic polymer resist material layer 2 are removed to obtain the patterned substrate material 1 in which the window 1f is formed on the recess 1b as shown in Fig. 3g.

- In both the embodiments mentioned above, the organic polymer resist material layer having the first desired pattern as well as the inorganic resist material layer possessing the second desired pattern have merely been utilized as an etching mask for patterning the substrate material being a material to be worked, and finally both the resist material layers have been removed off. However it is possible that the organic polymer resist material layer formed on the substrate material is left as it stands without removing the resist material layer, and such layer is functionally utilized as a constitutional element of semiconductor devices. As a typical example, such manner is applicable for a formation of an interlayer insulation used for multilevel interconnection in integrated circuits and the like.

Figs. 4a-4j are sectional views each showing each stage of an embodiment in the case as mentioned above. As shown in Fig. 4a, a substrate material 5 has such a construction that an insulation layer 5b made of  $\text{SiO}_2$  is formed on the main surface of a semiconductor wafer made of silicon, and conductor layers 5c and 5d consisting of, for example, Al, polycrystal silicon, molybdenum or the like are disposed thereon.

- In the case where the main surface of such type of the substrate material 5 as described above is patterned with an upper layer which is, for example, electrically insulated from the conductor layer 5c by means of an interlayer insulation layer, while contacts with the conductor layer 5d, and is extended from a position on the interlayer insulation layer to that on the aforesaid insulation layer 5b, the organic polymer resist material layer 2 is first applied on the whole surface of the substrate material as shown in Fig. 4b. As the organic polymer resist material layer 2, any resist material disclosed in the above-mentioned embodiments may be employed, and among others a resist containing cyclized polybutadiene rubber as the principal constituent is particularly preferable in such point that electrical properties as an interlayer insulation layer, more specifically insulation resistance and dielectric loss property are excellent. Then, as shown in Fig. 4c, the organic polymer resist material layer 2 is patterned in accordance with an usual manner so as to establish the pattern as an interlayer insulation layer. Then a similar heat treatment to that in the embodiment mentioned previously follows, so that the patterned

organic polymer resist material layer 2 is cured.

Thereafter, as shown in Fig. 4d, the inorganic resist material layer 3 is formed on the organic polymer resist material layer 2 and the insulating layer 5b so as to cover the whole surface of the organic polymer resist material layer 2 and exposed portions of the insulation layer 5b on the main surface of the substrate material 5, and then, as shown in Fig. 4e, exposure is made by means of the light or accelerated particle beam 4 like electron beam with a pattern by which a window can be provided on the resist material layer positioned on the conductor layer 5d. Then as shown in Fig. 4f, the inorganic resist material layer 3 is developed and further the organic polymer resist material layer 2 is etched as shown in Fig. 4g, and the inorganic resist material layer 3 is then removed as shown in Fig. 4h. Next, the upper conductor layer 6 is formed on the patterned organic polymer resist material layer 2 and the insulation layer 5b so as to cover the whole surface of the patterned organic polymer resist material layer 2 and exposed portions of the insulation layer 5b on the main surface of the substrate material 5 as shown in Fig. 4i, and finally the substrate material thus treated is formed in accordance with a publicly known manner to establish a desired pattern, so that a pattern possessing two conductor layers involving the aforesaid organic polymer resist material layer 2 as the interlayer insulation layer is formed as shown in Fig. 4j.

Although the above third embodiment has been described in connection with two-layer pattern, multilevel pattern including three or more layers can, of course, easily be formed by repeating the process steps as mentioned above.

The method of pattern formation according to the present invention is also very effective for formation of a thin film pattern in accordance with a so-called lift-off method. For instance, in the case where a fine thin film pattern is formed on a recess in the main surface of a nonplanar substrate material 7 as shown in Figs. 5a-5c, such pattern formation that the whole surface of the recess is covered with the organic polymer resist material layer 2 and a fine pattern formation by means of the inorganic resist material layer 3 are similarly carried out as in the embodiment described above, and then the aforesaid organic polymer resist material layer 2 is subjected to an etching treatment by utilizing the silver doped region 3c in the inorganic resist material layer 3 for forming the aforesaid fine pattern as the mask as shown in Fig. 5a. Then a desired thin film layer 8 is formed so as to cover the inorganic resist material layer 3 and the whole main surface of the substrate material 7 as shown in Fig. 5b, and finally when the organic polymer resist material layer 2 and the inorganic resist material layer 3 are removed, the thin film layer 8 on the aforesaid inorganic resist material layer 3 is simultaneously removed therewith, whereby a desired thin film pattern is formed as shown in Fig. 5c.

It is to be noted that even if the process steps in the above fourth embodiment are somewhat modified, it is possible to obtain a similar thin film pattern. For instance, as shown in Fig. 5a, a fine pattern with the

inorganic resist material layer 3 is transferred to the organic polymer resist material layer 2, then only the inorganic resist material layer 3 is removed as shown in Fig. 6a, a thin film layer 8 is then formed on the organic polymer resist material layer 2 and the main surface of the substrate material 7 which is not covered with the above organic polymer resist material layer 2 as shown in Fig. 6b, and then the organic polymer resist material layer 2 is removed together with the thin film layer 8 thereon, whereby a desired thin film pattern is formed as shown in Fig. 6c. Such manner as stated above is effective for the formation of a relief including a large and small patterns.

As described above, since the method of pattern formation of this invention comprises the steps of forming a first desired pattern with an organic polymer resist material layer, heat-treating the patterned organic polymer resist material layer, then forming an inorganic resist material layer on said patterned organic polymer resist material layer to cover the whole surface thereof, further forming a second desired pattern with the aforesaid inorganic resist material layer, and thereafter transferring the resulting second desired pattern to the aforesaid organic polymer resist material layer, the method according to the invention has the following various excellent advantages.

First, the first desired pattern formed with the organic polymer resist material layer aims at covering and flattening of the whole nonplanar assembled portions of a substrate material, of formation of a relatively large pattern. Accordingly, a high accuracy in pattern is not required, so that it is possible that a film thickness of the organic polymer resist material layer in the invention is very thickened as compared with a case of the pattern formation with only a conventional organic polymer resist material layer. For this reason, etching resistance increases when such organic polymer resist material layer is utilized as a mask for effecting etching treatment of a substrate material. As a consequence, various advantages such that an applicable extent of substrate material as a material to be worked expands, that applicable etchants and etching gas become diversified, and that fine and deep etching become possible can be achieved.

Besides the increase in a film thickness of organic polymer resist material layer as mentioned above as well as the heat treatment after pattern formation of the aforesaid organic polymer resist material layer are very effective for flattening nonplanar portions of a substrate material, and this fact closely relates to improvement of accuracy in the formed pattern in the succeeding step for forming the pattern with an inorganic resist material layer. As a result, it becomes very easy to establish a fine pattern formation with a high accuracy on the surface of a substrate having remarkable nonplanar portions on which a precise pattern could have hardly been formed heretofore, so that high resolution characteristic involved in an organic resist material layer can effectively be utilized. Furthermore, as mentioned above, increase of the film thickness of a resist mask is easy, besides the method of this invention is very effective for the formation of a mask with

high accuracy for, for example, implantation of high energy ion, or for ion beam etching of a strong etch resistive material such as  $\text{LiNbO}_3$  or the like.

In addition, when manners of the method according to the present invention are functionally divided in such that a relatively large pattern is formed with an organic polymer resist material layer, whilst a fine pattern is formed with an inorganic resist material layer, the exposure source, manner for exposure or the like in case of exposing each pattern can be changed. Thus, when the manner of exposure is selected in accordance with a required accuracy in each pattern formation, in such that, for example, light of electron beam is utilized for the large and fine patterns, respectively, the required accuracy can be maintained, besides the exposure time can remarkably be reduced as compared with the case where all the patterns are exposed by means of electron beam, so that throughput can be increased.

Moreover, according to the present invention, when a pattern is formed on an organic polymer resist material layer in response to an alignment mark for the alignment of a mask, only a marked portion can be exposed. Therefore, such disadvantageous problem that the reflected light from a mask cannot be detected in a method of pattern formation in which a bilayer resists is employed can be dissolved, so that the automation for the alignment of mask in a light exposure system can be attained.

Besides various combinations of the process steps are possible in the present invention, for instance, deep and shallow etching treatments upon a substrate to be worked can efficiently be carried out, and such manner is effective in the case where a film thickness of a layer to be worked is different in different portions in the surface of a wafer and a pattern is formed on such layer to be worked, so that it results in simplification of process steps.

In accordance with the present invention, since the organic polymer resist material layer formed on the substrate material is sufficiently cured during a heat-treating stage after the formation of a pattern, various properties such as hardness, electrical properties, heat resistance and the like are improved, so that the method of the invention becomes very advantageous for formation of an interlayer insulation layer and application of lift-off method. In this respect, the description will be made hereinbelow in more detail.

Interlayer insulation films made of polymer materials including polyimide series resin as a typical example are known, but these films usually have no photosensitivity, i.e., pattern forming function. As the polymer resist materials satisfying characteristic properties of interlayer insulation film, the aforesaid cyclized polybutadiene series resists are known, and when such resists are utilized as the organic polymer resist material layers in the method of the present invention, the following advantages can be expected. That is, there are many cases where fineness and high accuracy are required for an interlayer film through-hole working, but since the working of organic polymer resist material layer as the interlayer insulation film is carried out in accordance with a reactive ion etching manner by utilizing an inor-

ganic resist mask in the present invention, the required fineness can sufficiently be satisfied. However, in this case, a patterned section of the organic polymer resist material layer comes to be rectangular, and it results in such phenomenon that a conductor hardly enters such narrow rectangular gap between the patterns at the time of forming the conductor layer, so that such phenomenon becomes a cause for breaking the stepped surface of the upper conductor. According to the present invention, since a pattern is formed with an organic polymer resist material layer, a section of the pattern possesses inclined surfaces as shown in the layer 2 of, for example, Fig. 1b. A fine pattern having a rectangular section is formed with an inorganic resist on such patterned organic polymer resist material layer in accordance with a reactive ion etching manner, and then an upper conductor layer is applied on the patterned organic polymer resist material layer having such fine pattern, whereby two-layer conductors involving the organic polymer resist material layer as the interlayer insulation film can be formed. Besides this manner in the present invention is also effective for flattening one layer of the resist surface in a two-layer resist technique. In addition, since a pattern is formed with an organic polymer resist material layer in the present invention, flexibility increases in respect of construction and design for the pattern of interlayer film.

In case of applying the present invention to a method of the formation for an ion implantation mask, a mask having two kinds of ion stopping abilities can be formed, so that a simultaneous formation of two kinds of implantation regions can be made by ion implantation.

According to the present invention, as described above, function of pattern formation is given to an organic polymer resist material layer, so that many advantages which cannot be attained by a mere two-layer resist technique can be realized, besides problems involved in two-layer resist are also dissolved. Particularly, when the method of the present invention is practised by modifying variously the pattern formation processes thereof, the invention is widely applicable for various patterns, layer constructions and layer materials.

#### CLAIMS

1. A method of pattern formation, which comprises the steps of:

- forming a first desired pattern consisting of an organic polymer resist material layer on the surface of layer to be worked of a substrate material, applying a heat treatment to the patterned organic polymer resist material layer,
- forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver on the organic polymer resists material layer thus heat-treated so as to cover the whole surface thereof,
- forming a second desired pattern with said inorganic resist material layer,
- etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer,

applying an etching treatment to said layer to be worked in a region which is not covered with said organic polymer resist material layer, and removing said inorganic and organic polymer resist material layers.

2. A method of pattern formation as defined in claim 1, wherein said organic polymer resist material layer is made from a resist material comprising cyclized polybutadiene rubber as the principal constituent.

3. A method of pattern formation as defined in claim 1, wherein said selenium-based glass material layer is made from a glass material comprising selenium and germanium as the principal constituents.

4. A method of pattern formation, which comprises the steps of:

forming a first desired pattern consisting of an organic polymer resist material layer on the surface of layer to be worked of a substrate material, applying a heat treatment to the patterned organic polymer resist material layer, forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver on the organic polymer resist material layer thus heat-treated so as to cover the whole surface thereof,

forming a second desired pattern with said inorganic resist material layer, etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer, removing said inorganic resist material layer, applying an etching treatment to said layer to be worked in a region which is not covered with said organic polymer resist material layer, and removing said organic polymer resist material layer.

5. A method of pattern formation as defined in claim 4, wherein said organic polymer resist material layer is made from a resist material comprising cyclized polybutadiene rubber as the principal constituent.

6. A method of pattern formation as defined in claim 4, wherein said selenium-based glass material layer is made from a glass material comprising selenium and germanium as the principal constituents.

7. A method of pattern formation, which comprises the steps of:

forming a first desired pattern consisting of an organic polymer resist material layer on the surface of layer to be worked of a substrate material, applying a heat treatment to the patterned organic polymer resist material layer, etching to remove said layer to be worked in a region which is not covered with said patterned organic polymer resist material layer,

forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver on the organic polymer resist material layer thus heat-treated and the exposed layer to be worked by means of said etching treatment so as to cover the

whole surface of said organic polymer resist material layer and the surface of said exposed layer to be worked,

forming a second desired pattern with said inorganic resist material layer,

etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer,

applying an etching treatment to said layer to be worked in a region which is not covered with said organic polymer resist material layer, and removing said inorganic and organic polymer resist material layers.

8. A method of pattern formation as defined in claim 7, wherein said organic polymer resist material layer is made from a resist material comprising cyclized polybutadiene rubber as the principal constituent.

9. A method of pattern formation as defined in claim 7, wherein said selenium-based glass material layer is made from a glass material comprising selenium and germanium as the principal constituents.

10. A method of pattern formation, which comprises the steps of:

forming a first desired pattern consisting of an organic polymer resist material layer on the surface of layer to be worked of a substrate material provided with a patterned conductor layer, applying a heat treatment to said patterned organic polymer resist material layer, forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver on the organic polymer resist material layer thus heat-treated so as to cover the whole surface thereof,

forming a second desired pattern with said inorganic resist material layer,

etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer,

removing said inorganic resist material layer, and forming a third desired pattern consisting of a conductor layer on said organic polymer resist material layer and said surface of layer to be worked of the substrate material in a region which is not covered with said organic polymer resist material layer.

11. A method of pattern formation as defined in claim 10, wherein said organic polymer resist material layer is made from a resist material comprising cyclized polybutadiene rubber as the principal constituent.

12. A method of pattern formation as defined in claim 10, wherein said selenium-based glass material layer is made from a glass material comprising selenium and germanium as the principal constituents.

13. A method of pattern formation, which comprises the steps of:

forming a first desired pattern consisting of organic polymer resist material layer on the surface of layer to be worked of a substrate material,

applying a heat treatment to the patterned organic

polymer resist material layer,  
forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver  
5 on the organic polymer resist material layer thus heat-treated so as to cover the whole surface thereof,

forming a second desired pattern with said inorganic resist material layer,

10 etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer,

forming a thin film layer on said inorganic resist material layer and said surface of layer to be worked

15 of the substrate material in a region which is not covered with said organic polymer resist material layer, and

removing said inorganic and organic polymer resist material layer together with said thin film layer  
20 formed on said inorganic resist material layer.

14. A method of pattern formation as defined in claim 13, wherein said organic polymer resist material layer is made from a resist material comprising cyclized polybutadiene rubber as the principal constituent.

15. A method of pattern formation as defined in claim 13, wherein said selenium-based glass material layer is made from a glass material comprising selenium and germanium as the principal constituents.  
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16. A method of pattern formation, which comprises the steps of:

forming a first desired pattern consisting of organic polymer resist material layer on the surface  
35 of layer to be worked of a substrate material,

applying a heat treatment to the patterned organic polymer resist material layer,

forming an inorganic resist material layer being a laminate consisting of a selenium-based glass material layer and a silver layer or layer containing silver  
40 on the organic polymer resist material layer thus heat-treated so as to cover the whole surface thereof,

forming a second desired pattern with said inorganic resist material layer,  
45

etching to remove the organic polymer resist material layer in a region which is not covered with the patterned inorganic resist material layer,

removing said inorganic resist material layer,  
50 forming a thin film layer on said organic polymer resist material layer and said surface of layer to be worked of the substrate material in a region which is not covered with said organic polymer resist material layer, and

55 removing said organic polymer resist material layer together with said thin film layer formed thereon.

17. A method of pattern formation as defined in claim 16, wherein said organic polymer resist material layer is made from a resist material comprising cyclized polybutadiene rubber as the principal constituent.  
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18. A method of pattern formation as defined in claim 16, wherein said selenium-based glass material layer is made from a glass material comprising  
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selenium and germanium as the principal constituents.

19. A method of pattern formation substantially as hereinbefore described with reference to and as  
70 illustrated in the accompanying drawings.

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